

SCIENCE FOR CERAMIC PRODUCTION

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PRODUCTION OF TRANSPARENT CERAMIC. SYNERGETIC APPROACH

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A systems approach to obtaining high-quality transparent ceramic is examined from the standpoint of synergetics. The optimal decrease of the degree of nonequilibrium of the system must be attained at all stages of fabrication of transparent ceramic: during preparation of the powder including its synthesis, introduction of densifying additives, and heat treatment. The formation of aggregates and local densification with strong solid-state bridges between particles, as a result of which pores enter the crystal, must be prevented during the preparation of the molding mix, molding, and removal of the binder as well as during sintering.

Key words: transparent ceramic, technology, synergetics.

Transparent ceramics (transparent polycrystalline materials), whose light transmission is second to that of single crystals, as a rule, have superior heat-resistance and sometimes even strength and are less expensive, especially if the shape of the article is complex [1 – 2]. This explains the growing interest in such materials for use in optics and laser technology. To attain transparency the ceramic must be non-porous and have optically perfect crystals and crystal boundaries. A large number of pores, even very small ones, make the ceramic opaque, since their surfaces intensively reflect and refract light. The pores can be inter- and intracrystalline. Intercrystalline pores are much easier to remove, since the crystal boundaries are vacancy sinks, facilitating their removal by means of separate vacancies. If the principal phase is optically isotropic (cubic), then this facilitates obtaining transparent ceramics, since there is no optical nonuniformity associated with the difference of the orientation of neighboring crystals.

The removal of intracrystalline pores, even if they are submicron in size, is a much longer process. Intracrystalline pores can acquire equilibrium faceting [3], which makes it much more difficult to remove them. Impurities forming a gas phase during heat treatment and producing excess pressure inside closed pores help to preserve intracrystalline pores. Impurities that can accelerate diffusion processes, leading to pores acquiring equilibrium faceting, are concentrated on the surfaces of pores.

Crystal boundaries must be thin and be structurally as perfect as possible. The presence of a second phase, whose optical properties are different from those of the principal phase, on the boundaries results in reflection and refraction of light, which decreases the transparency of the ceramic. For this reason, highly pure initial materials are used to obtain a transparent ceramic, and the amount of additive is determined so that all of it enters into a solid solution with the principal phase.

It is known that the effectiveness of dopants (modifying additives) increases with increasing purity of the principal material. This is because impurities mutually compensate their effect on the formation of vacancies, which play a determining role in diffusion mass transfer during sintering of the ceramic (in the presence of Schottky disorder). For this reason, the purity of the principal phase of transparent ceramic must be as high as possible.

The crystals in the ceramics must be optically perfect. The main requirement is that there can be no optical imperfections: pores, inclusions of a second solid phase, block boundaries, dislocations. In a ceramic consisting of optically anisotropic crystals (noncubic system), additional light scattering arises at the boundaries because of their arbitrary crystallographic orientation [1].

Mass transfer, which plays a determining role in the production (especially sintering) of transparent ceramic, is a typical irreversible and nonequilibrium process. Such processes are studied in the physics (thermodynamics) of open systems, thermodynamics of irreversible processes, and syner-

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getics, which are synonyms with respect to physical – chemical systems. Synergetics focuses on self-organization phenomena. Open systems exchange matter with the environment (matter, energy, and information). Irreversible and nonequilibrium process are present in all real (open) ceramic systems and at different structural levels. In thermodynamics a region of space separated from the surrounding space, called external, or surrounding medium by a real or imaginary boundary is said to be a system. The concepts “system” and “surrounding medium” depend on the scale chosen. For an atom and a vacancy the surrounding medium are the neighboring atoms and vacancies, for powder particles it is the surrounding phase, and for a fired ceramic blank it is the furnace space surrounding it.

An ensemble of particles forms a system which in synergetics is called an active medium. The behavior of the system of particles in different alterations of ceramic technology is accompanied by a change of structure. The structure changes at different scales, successively passing through stable and unstable states [4]. When matter is delivered to an open system corresponding structures are formed (self-organization) for dispersal of the matter into the surrounding medium or accumulation of the matter in itself (accumulating structures); this depends substantially on the degree of nonequilibrium of the system with a given process [5]. It should be noted that depending on the situation one and the same structures can be dissipative or accumulating, so that the division is quite arbitrary. A classical example of a dissipative structure are Bénard cells (vortices), arising with unidirectional transfer of heat to a layer of liquid placed between horizontal glass plates [6]. For a definite temperature gradient between the plates the molecules of the liquid self-organize into vortices, which enable intense heat transfer through the layer of liquid into the surrounding medium. A Bénard vortex enables heat transfer on the cold side of the layer of liquid into the surrounding medium, so that it is said to be a dissipative structure. At the same time, on the hot boundary it absorbs heat from the surrounding medium into the system and retains it there during transfer to the cold wall. In this sense it should be regarded as an accumulating system.

The system strives to use as dissipative or accumulating structural elements which are already present in it, and it creates new ones only if they are not present at all or there are too few of them [5]. This is graphically shown in the elimination of “gathering” defects in glazes, when preliminary separation of a deposited unfired layer of glaze into squares of a definite size was used successfully [7]. For the correct choice of the size of the squares, the system uses them and does not spontaneously create new ones of arbitrary size, which result in “gathering.”

The situation where a transition occurs from an unstable into a stable state, when two equivalent final states into which the system can transition exist, is distinguished in mathematics. In this case one talks about a bifurcation (branching) of the process and the transition point, i.e., the

instability, is called a bifurcation point. The foundations of the mathematical theory of bifurcations were laid by A. Poincaré and A. N. Lyapunov and elaborated by A. A. Andronov and his school. In mathematics a bifurcation means a change of the topological structure of the partition of the phase space of a dynamical system into trajectories with a small change of the parameters of the system [8]. The theory of bifurcations makes it possible to represent all of the principal qualitative features of the solutions of a system of differential equations without integrating the system.

From the standpoint of mathematics such a situation is formally observed in cases where the solution of a nonlinear equation describing a process becomes unstable, and the system then transitions from one solution to two new solutions (mathematically, this results in a change of the symmetry of the solution). It is important that these two new states for the developing system are equivalent and a choice of one of them is made randomly depending on small external perturbations or internal fluctuations. In a complex situation which is described by a set of such equations there can exist many stable states of the system, one of which the system passes into randomly after becoming unstable as a result of perturbations or fluctuations; then one talks about multistability. There also exists a different point of view according to which a bifurcation is a helpful idealization, but it is more accurate to talk about instability and unstable states. Such a position is more practical, since there is no need to prove the existence of two equivalent states of the system. In reality, a pure bifurcation is encountered extremely rarely. Ordinarily, one of the states at the proposed bifurcation point is preferable for reasons which are external or internal for the system.

In the course of its evolution a system (fired blank) can occupy different stable states with substantially different properties. Then the properties of the articles obtained will also differ substantially. Thus, multistability with stable states whose properties are substantially different is responsible for the low reproducibility of the properties of the articles. If the properties of the stable states are close and satisfy the requirements for the quality of the material, then this is entirely acceptable. However, if the differences with respect to the properties are not acceptable, then such multistability must be eliminated, which is accomplished by different technological devices.

A stable state of a system is a dynamical equilibrium and is accompanied by a continual exchange of matter with the external medium. In an unstable state, systems are highly sensitive to different actions. The evolution of a system can be made more predictable by acting on the system in an unstable state by means of internal or external controlling actions, the role of internal actions being played by preceding structural elements created in the material at preceding technological stages [5, 7].

All real processes are accompanied by a transition through a multitude of unstable states. Their number sharply increases as the state of the system passes from the macroscopic level to the atomic level, so that a hierarchy of unsta-

ble states arises. The principal states are unstable states which have a definite effect on the subsequent evolution of the structure of the ceramic. Technologists know very well that in technological processes there are regions where the parameters must be monitored especially strictly in order to obtain products with the required properties. In other regions these requirements are less stringent. In this sense the problem for technologists is to find the principle unstable state and influence the system in these states (for example, the blank being fired) using external or internal controlling actions in a manner ensuring that the structure of the ceramic evolves in the desired direction [9]. The possibility of finding conditions under which a system in an unstable state itself creates the desired structure via self-organization is not ruled out. Such a global approach on the basis of the principles of synergetics will help technologists to gain a deeper understanding of the processes occurring and approach the creation of structures ensuring the required properties in a better grounded manner.

The properties of ceramic materials are determined by their structure. The structure of a ceramic is taken to mean the size, shape, relative arrangement, and quantitative relations of its constituent elements, which possess a definite chemical and phase composition. The following structures are distinguished depending on the characteristic size of an element: macrostructure (> 1 mm, right up to the article as whole), microstructure ($1 - 10^{-3}$ mm), and substructure ($< 10^{-3}$ mm, right down to electrons and smaller particles) [10]. It should be especially noted that for such an analysis the chemical composition is included in the concept "structure" at the level of the substructure, since atoms are also distinguished by structure. Mass exchange with the surrounding medium incorporates scales from chemical bonds (substructure) to the entire sample (macrostructure). The hierarchical nature of such a division makes it possible to represent mass exchange between the system (a distinguished structural element) and the surrounding medium by structural elements of different sizes. During mass transfer the structure of the system and the surrounding medium changes; dissipative and accumulating structures arise. In mass flow crossing the boundary of the system, self-organization processes can also occur, specifically, the merging of elements into larger elements or breakup of elements into smaller ones.

In the technology of ceramics, manifestations of self-organization are encountered at various stages: during the preparation of powder, molding mixes, molding, removal of the temporary technological binder, and sintering. From the standpoint of synergetics the requirements for the technologists for preparing transparent ceramic can be formulated as follows. The prerequisites for the formation of undesirable accumulating structures, which are intra-crystalline pores and precipitates of a second solid phase on boundaries and inside crystals, must be eliminated at all stages of the technology (obtaining ceramic powders, molding, removal of the temporary technological binder, firing).

All stages are important in the technology of any ceramic. Structures which are created at preceding stages play the role in internal controlling actions for subsequent stages, which is referred to as the influence of the past history. This is especially valid for transparent ceramic.

Ordinarily, ultradisperse and even nanosize powders are used to obtain transparent ceramic. A system consisting of such powders decreases its surface energy by aggregation. The formation of aggregates can be called a dissipative structure, which lower the energy of the system, as well as an accumulating structure, which stores part of the energy inside an aggregate in the form of pores and boundaries between particles. The appearance of pores and interparticle solid-state bridges is considered to be undesirable, since the subsequent evolution of the structure of such an aggregate during sintering often results in the aggregate converting into a single crystal with internal pores and loss of transparency. To make such aggregates less likely to appear, surfactants are used, water is replaced with an organic medium or an azeotropic mixture with water, the water is rapidly frozen, the ice is removed in the solid phase, the process is conducted under supercritical conditions, and disaggregation is performed, for example, by mechanical milling or vibrational, acoustic or ultrasonic working.

Preliminary heat-treatment of the powder at temperatures where mass transfer becomes appreciable is an effective method of decreasing the activity of particles with respect to diffusion mass transfer during sintering. Diffusion mass transfer in this case leads to perfection of the structure of crystals at the sublevel. During the subsequent sintering this slows mass transfer through the boundary of the crystals and decreases the probability of pore capture by crystals.

Aggregation processes occur not only during the preparation of highly disperse powder but also during the preparation of molding mixes, molding, and sintering. A large departure from equilibrium of the system (molded and sintered powder) during these processes creates the prerequisites for the formation of denser regions adjoining less dense regions. The denser regions, arising in a blank when it is molded by different methods and at the initial stages of sintering, are called regions of local densification or simply local densification. They can also evolve into large crystals with intracrystalline pores, which do not permit obtaining high transparency because of the difficulty of removing them. It is known that granulation has a large positive effect, when dense aggregates of the same size but without solid-state bridges between the constituent particles are prepared from highly disperse powder. Granulated powders, playing the role of an internal controlling action, promote evolution of the structure of the blank into a denser structure with uniform density.

It is known that firing is the stage at which the final structure of the ceramic is formed. From the standpoint of synergetics firing a transparent oxide ceramic made from highly disperse powders is accompanied by a transition through three regions of the principal unstable states (non-

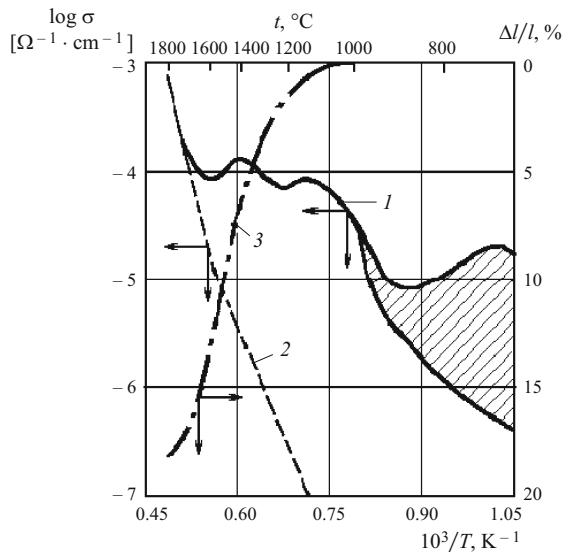


Fig. 1. Electric conductivity σ [(1) heating, (2) cooling] and shrinkage $\Delta l/l_0$ (3) of compacts formed from corundum during sintering. The hatching marks the region of nonreproducible values with the first heating of a compact [14].

equilibrium phase transitions — NPTs) [11, 12]. Even though they manifest features characteristic of bifurcations, we shall call them unstable states so as not to prove that they are actually bifurcations.

The first principal unstable state appears during firing at a temperature where smoothing of the character of a shear surface is observed. This can be recorded using a binocular magnifying glass with lateral illumination of the shear surface [13]. In this region the system (fired blank) manifests features of bifurcation, i.e., “loss of memory” of the preceding regions of local densification is observed, while new regions appear after it. The uncontrollable formation in this region of new local densification decreases the reproducibility of the structure and the properties associated with it. The reason for the often observed low level of reproducibility, for example, strength properties of ceramic obtained from highly disperse powders, lies precisely in local densification. The first maximum (NPT) on the curve of the electric conductivity of the heated compact (Fig. 1), presented in [14], approximately corresponds to this region. The first NPT is mainly associated with perfection of the structure with monovacancies, which form as a result of impurity atoms, first and foremost hydroxyl groups, which are sorbed and dissolved in regions near the surface, emerge at the surface of a crystal. The process is accompanied by a decrease of the concentration of the carriers and decreases the electric conductivity. The size of the crystal does not increase. As a result of diffusion mass transfer near the surface the crystals become more rounded. This facilitates the relaxation of stresses, which are a consequence of the regions of local densification that arise in the blank, and could be responsible for the smoothing of shear surfaces.

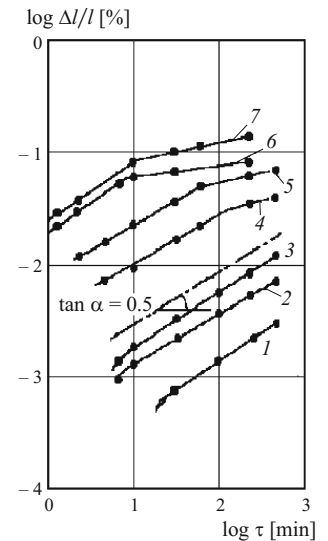


Fig. 2. Shrinkage isotherms of corundum compacts at temperatures 1000 (1), 1070 (2), 1150 (3), 1260 (4), 1360 (5), 1660 (6), and 1530°C (7) [14].

Vacancies emerge at the surface of crystals, lowering the friction between them, which subsequently leads to the onset of shrinkage. As the degree of departure from equilibrium near the first NPT increases (as the surface becomes less fractal) an increasingly larger part of the energy must be accumulated in near-surface layers in the form of associates of vacancies, for example, molecular and larger pores. For sintering of corundum this can be written as



For sintering “with controllable rate of shrinkage” soaking is done in this temperature range and the temperature is even lowered somewhat [15]. Ordinarily, blanks are heated to approximately the same temperatures during burnout of the temporary technological binder. To eliminate certain properties of bifurcations it is best to use external controlling signals, for example, an ultrasonic field, acoustic oscillations, and so on.

The second principal unstable state during sintering of oxides is observed at the maximum rate of shrinkage of the sample (inflection in the shrinkage curve, maximum on the differential shrinkage curve). On the curve of the electric conductivity of a heated compact it, evidently, corresponds to the second maximum in Fig. 1 (second NPT). The plastic deformation of the framework, controlled by mass transfer because of the volume diffusion, changes the structure of the blank.

Just as at the first NPT the process is limited by the volume diffusion of vacancies. This is confirmed by the tangent of the slope angle of the function

$$\log \Delta l/l_0 - \log \tau,$$

where $\Delta l/l_0$ is the shrinkage and τ is the isothermal soaking time, equal to 0.5 (Fig. 2) [14].

The sources of monovacancies are various nonequilibrium structural defects (substructure), and the sink is the matter at the boundary of a crystal. The emergence of vacan-

cies in the surface layer decreases the friction between the crystals. Under these conditions the surface tension forces become strong enough to give rise to substantial plastic deformation of the sample and intense shrinkage is observed. At the second NFT, in the course of plastic deformation during shrinkage, the structure is perfected and point defects (monovacancies) move to the surface of the crystals. The number of monovacancies decreases sharply, and the electric conductivity decreases. This process is associated, to a lesser degree, with the initial size of the particles, since the properties of the surface are largely nullified at the transition through the first maximum. The fewer particles there are, the more the structure is perfected at the first NFT (the higher the maximum).

Ordinarily, pressure during hot pressing is applied in the region of the second unstable state (elimination of the instability by means of an external action). In the temperature range of intense shrinkage the rate of temperature increase is decreased or soaking is performed [16] (providing the conditions for inheritance of the structure).

The third principal bifurcation (third NFT) in the production of high-density ceramic is associated with the change of the structure of an infinite cluster from open pores (onset of a transition of some open pores into closed pores). The evolution of the framework also passes through a region which is characteristic of a bifurcation (third maximum in Fig. 1), after which rapid growth of crystals is observed in the ceramic.

Technologists have long known of the rapid growth of crystals after a definite porosity is reached (approximately 10% of the total porosity). To obtain nonporous transparent ceramic from highly disperse powders crystal growth must start after the largest possible relative density of the blank is reached [17]. Such behavior of the system is obtained by adjusting the corresponding densifying additives (dopants), preliminary heat treatment of the highly disperse powder to decrease its sintering activity. In the language of synergetics this is the conservation of the topological structure of an infinite cluster of open pores by elimination of the bifurcation by means of internal signals — dopants and particle structure.

A number of processes, which can be understood by using a quasichemical approach, occur at the submicron level in oxides at the time they are fired. The predominant evaporation of oxygen at high temperatures gives rise to a protection response of the system in the form of the formation of a potential barrier on the boundary of a crystal as result of the elevated concentration of oxygen vacancies there. The presence of such a barrier impedes diffusion growth of crystals [11]. At the same time a high concentration of vacancies leads to instability of the crystal structure of the material at the boundary of crystals and facilitates its plastic deformation. The height of this concentration barrier depends on the energy characteristics (fractal structure) of a given section of the surface. The faster and the more oxygen anions evaporate from the boundary of a crystal, the higher the concentration barrier will be.

The barrier impedes further evaporation of oxygen and mass transfer through the boundary, i.e., crystal growth. For mass transfer in oxides, the motion of anions and cations must be balanced, and the motion of the slowest ions will control the process. The total electric current must be zero. In the vacancy mechanism of diffusion the vacancies whose concentration is lowest compared with the required concentration, will control mass transfer. In most oxides cation vacancies play this role during sintering [18].

The distortions of the crystal structure in the near-surface layer, through which the diffusion path passes, accelerate the structure-improving diffusion processes in it. A high concentration of vacancies in the near-surface layer of a crystal, for example, Al_2O_3 , causes oxygen vacancies to combine with cation vacancies, forming electrically neutral associates — molecular pores (see the reaction presented).

Evidently, the concentration barrier for oxygen monovacancies does not work on such associates. These associates overcome the concentration barrier, emerge at the boundary, which is a sink for vacancies, and annihilate in open pores in the course of plastic deformation during shrinkage. This process proceeds intensively, while the system of boundaries allows for removal of molecular pores onto the surface of the sample. An infinite cluster of open pores, which is connected with the surface of the blank, is most effective for this. This could explain a well-known fact: during sintering crystals undergo practically no growth before a definite minimum total porosity is reached (about 10%). The process of structural change of an infinite cluster of open pores after some of them have become closed pores corresponds to the third principal unstable state.

An infinite cluster of open pores in a separate part of a sintered blank transforms into regions isolated from the surface — closed pores. Their formation combined with perfection of the near-surface layers of crystals and intercrystal boundaries impedes predominant evaporation of oxygen from the surface layers of crystals. This decreases the concentration of nonstoichiometric oxygen vacancies in a near-surface layer and the oxygen diffusion rate. As result, on recrystallization of a dense ceramic it can drop below that of cations [19]. The concentration barrier for oxygen monovacancies on the surface of crystals decreases to such an extent that they start to overcome it in the required ratio with cation vacancies, engendering mass transfer and crystal growth. In addition, a decrease of the shrinkage rate and correspondingly the intensity of plastic deformations make it impossible to use the mechanism of vacancy annihilation in open pores effectively. Plastic deformations break up aggregates and local densification. The role of plastic deformations is maintained by the fact that when using highly disperse powders it is often possible to obtain a denser ceramic from less dense blanks, where plastic deformation on shrinkage is larger [20].

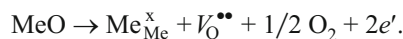
If the degree of nonequilibrium is such that there is not enough time for the system to remove all molecular pores, then closed pores begin to play the role of sinks. Then crystal

growth starts long before all molecular pores are removed, and it is impossible to obtain transparent ceramic. The presence of pores in sintered ceramic is an example of energy accumulation in the form of new surfaces.

Additives that retard diffusion mass transfer are used as internal controlling actions to eliminate instability at the third NFT. Additives playing the role of internal controlling actions and having a definite effect on the structural evolution of a material are also used to obtain transparent ceramics. They regulate diffusion mass transfer and promote the removal of intra- and intercrystalline pores and perfection of the structure of boundaries and of the crystals themselves. The amount of additive is chosen so that after sintering is completed it does not precipitate in the form of a new solid phase but rather enters into a solid solution with the principal crystalline phase. In other words, the concentration of the additive must be less than the limit of its solubility in the principal phase at firing temperatures.

Additives should decrease the degree of nonequilibrium of the system during sintering, i.e., stop crystal growth and thereby slow the motion of crystal boundaries [21, 22]. Then, the system can use to the maximum extent possible by means of diffusion mass transfer the energy flowing in from the outside on uniform densification of the entire blank and not on the creation of accumulating structures in the form of pores. Then the probability of pore detachment from boundaries and transformation into intracrystalline pores is lower. In addition, additives should accelerate surface diffusion, so that pore removal along crystal boundaries is facilitated.

The defect formation reaction is used to choose additives [23]. We shall examine the principles of choosing additives for the example of obtaining a transparent ceramic from oxides. If diffusion in crystals proceeds by the vacancy mechanism, then the vacancies must be in the cationic sublattice (metal sublattice) and in the oxygen sublattice. In most oxides the oxygen volatility at sintering temperatures is higher than in metal. As a result, oxygen vacancies ($V_O^{\bullet\bullet}$) form in the oxygen sublattice, especially in the near-boundary layers of crystals:



An increase of the concentration oxygen vacancies $[V_O^{\bullet\bullet}]$ according to the equation

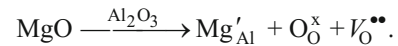
$$K_s = [V_{\text{Me}}''] [V_O^{\bullet\bullet}]$$

results in a decrease of the concentration of vacancies in the cation sublattice $[V_{\text{Me}}'']$ in accordance with Schottky's equation

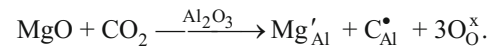


Thus, a deficit of V_{Me}'' arises. In complex compounds, specifically, in oxides, an adequate number of vacancies must be present in both sublattices.

Additives that give oxygen vacancies must be used to decrease the degree of nonequilibrium of the system (sintered blank). This will decrease the rate of diffusion mass transfer and increase the sintering temperature but decrease the probability of formation of accumulating structures in the form of pores and make it possible to obtain a transparent ceramic. So, MgO as an additive in the production of transparent ceramic from Al_2O_3 forms oxygen vacancies, which slow down diffusion mass transfer and pore capture by growing crystals:



It was shown that a transparent ceramic cannot be obtained if in obtaining Al_2O_3 by hydrolysis of alkoxides and introduction of densifying additives with water for hydrolysis carbon from the alkoxy groups remains in the material [24]. The color of the powder remained white, since carbon was in an oxidized state. Carbon cannot be removed by increasing the soaking time at high temperature in air. Carbon is removed in a reducing medium. The following reaction, where in contrast to the preceding one the introduction of magnesium cations is compensated by oxygen cations and no longer results in the appearance of oxygen vacancies, can be written conditionally:



As a result, due to the appearance of carbon cations in the lattice the concentration of oxygen vacancies decreases, diffusion mass transfer through the boundary of crystals accelerates, crystals trap pores, and transparency vanishes.

It should be noted that the description with the help of vacancies is a convenient idealization of the phenomenon associated with the weakening of chemical bonds in the material. Everything that leads to strengthening of the chemical bonds in the material will slow down diffusion mass transfer, and the weakening of chemical bonds will intensify it.

The mass-transfer situation changes if a layer of a second phase is present on the boundaries of crystals. If diffusion mass transfer through the second phase is small, then this will stop the growth of crystals and trapping of pores by them; if it is large, then pore trapping will be facilitated. So, the introduction into Y_2O_3 of a large quantity of additives, for example, Gd_2O_3 , which forms a wide region of solid solutions with Y_2O_3 , permits obtaining transparent ceramic [17]. At the initial stage of sintering a layer of Gd_2O_3 (solid solution of Y_2O_3 in Gd_2O_3) is present on the surface of Y_2O_3 crystals (solid solution of Gd_2O_3 in Y_2O_3). Here the chemical bonds in Y_2O_3 are weakened (with an increase of the lattice parameter because the radius of the Gd^{3+} ion is somewhat larger than that of Y^{3+}), which accelerates mass transfer within the crystal and increases the perfection of its structure. At the same time a layer consisting of a solid solution of Y_2O_3 in Gd_2O_3 blocks mass transfer through crystal boundaries. In this solid solution the situation is opposite to that in the interior regions of the crystals of the solid solution.

In obtaining high-density ceramic, technologists have established empirically the main unstable states and multistability. Synergetics opens paths toward a more systematic analysis of the technological processes and the development of materials with prescribed structure and properties. The manifestation of these three main unstable states intensifies with increasing nonequilibrium of the sintering process, i.e., with decreasing size of the particles of the powder used, especially when obtaining a nanoceramic.

Summarizing, we can say that to obtain a transparent ceramic it is necessary to make the correct choice of densifying additives, which would decrease the degree of nonequilibrium of the system (growing crystal) and decrease the probability of diffusion mass transfer through the boundaries of crystals. This eliminates the evolution of aggregates into large crystals with intracrystalline pores and trapping of intercrystalline pores by growing crystals. An additive can create oxygen vacancies (with Schottky disorder) and in this way stop diffusion mass transfer and decrease the degree of nonequilibrium of the system. Another possibility is distribution of an additive, over the surface of the particles, that blocks up to the final stage of sintering mass transfer through crystal boundaries and at the final state completely passes into a solid solution.

The formation of aggregates and local densification with strong solid-state bridges between particles, which allow pores to enter crystals, must be eliminated at the stages of powder preparation, including synthesis of the powder, introduction of densifying additives and heat-treatment for optimal reduction of its sintering activity, obtaining the molding mix, molding, and elimination of the binder. A regime of increasing temperature during firing should help attain this objective. The evolution of local densification in crystals with intracrystalline pores should not be allowed. Pores in the sintered blank must remain only between crystals, while the crystals must be pore-free. This is promoted by maintaining interlinked open pores to maximum relative density (infinite cluster of open pores). Such a systems approach opens paths for obtaining high-quality transparent ceramics.

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